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ABSTRACT

The decomposition of C₃H₈ and its reaction with CO₂ have been investigated on Au deposited on ZnO, MgO and Al₂O₃. The reactions proceeded above 650–700 K. The conversion of C₃H₈ was only few percents on Au/MgO and Au/Al₂O₃, even at 873 K, but reached ~17% on Au/ZnO. The selectivity of propylene formation was about 56%. CO₂ only slightly affected the reaction of C₃H₈ on Au/Al₂O₃ and Au/MgO, but significantly enhanced the conversion of C₃H₈ on Au/ZnO catalyst. The formation of large amount of CO indicates the involvement of CO₂ in the reaction of C₃H₈. From the product distribution it was inferred that beside the oxidative dehydrogenation and dry reforming reaction, the decomposition of C₃H₈ into CH₄ and surface carbon also occurred. The effect of ZnO is explained by an electronic interaction between n-type ZnO and Au particles leading to a formation of reactive CO₂⁻.

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1. Introduction

The production of synthesis gas, H₂ + CO, in the dry reforming of CH₄ is an important process for chemical technology and has been the subject of extensive studies [1–3]. From the first comparative work it was found that on the basis of turnover frequency determined on noble metals, Rh and Ru are the most active catalysts [4]. Attempts were also made to produce synthesis gas by the reactions of C₂H₆ and C₃H₈ with CO₂. Whereas in the absence of CO₂ the dehydrogenation of C₃H₈ was the major process, in the presence of CO₂ the formation of H₂ + CO₂ came into prominence [5–10]. As regards the dry reforming of C₃H₈, Rh and Ru also exhibited the highest specific activity [5]. Kinetic measurements revealed a zero-order dependence in C₃H₈ and a fractional dependence in CO₂ [6]. Many of the above cited studies revealed that the nature of the support plays an important role in the activity and selectivity of different catalysts. The best example is Mo₂C. Whereas Mo₂C/SiO₂ catalyzed the dehydrogenation of C₃H₈ [10], using ZSM-5 as a support the aromatization of C₃H₈ became the main reaction pathway [11]. Several studies have been also performed on the oxidative dehydrogenation of propane with molecular O₂ on oxide catalysts [12–15]. V₂O₅ containing catalysts proved to be the most effective and selective, particularly when C₃H₈ was in a great excess [14]. A great challenge was to avoid the over oxidation of olefins formed. The influence of several additives including Au/TiO₂ was tested [14]. Au/TiO₂ alone showed a low activity, but mixing with V₂O₅, yielded H₂ in larger concentration than obtained on

either vanadium or gold [14]. Au/TiO₂ was also active in the selective oxidation of propane to propylene oxide [15].

In the present work the reaction of C₃H₈ with CO₂ is examined over supported Au nanoparticles. As was discovered by several decades ago, Au in nanosize exhibits a surprisingly high activity in many catalytic reactions [16–18]. Recently, we found that Au nanoparticles supported by n-type semiconducting oxides are very effective catalysts in the reaction of C₂H₆ with CO₂ [19].

2. Experimental

2.1. Materials

Supported Au catalysts with a gold loading of 1 wt% were prepared by a deposition–precipitation method. Chloroauric acid (HAuCl₄·aq p.a. 49% Au, Fluka AG) was first dissolved in triply distilled water. After the pH of the HAuCl₄ aqueous solution was adjusted to 7.5 pH by adding 25% ammonia solution, the fine powder of oxidic support was suspended and kept at 343 K for 1 h with continuous stirring. The suspension was aged for 24 h at room temperature and washed with distilled water repeatedly, dried at 353 K, calcined in air and reduced at 673 K for 4 h. Al₂O₃ (Degussa) and MgO (Reanal) were applied as a support. 1% Au/ZnO (AUROLite) sample was purchased from Strem Chem. The gases used were of commercial purity.

2.2. Methods

For FTIR studies a mobile IR cell housed in a metal chamber was used, which can be evacuated to 10^{−5} Torr using a turbo molecular

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pumping system. Infrared spectra were recorded with a Biorad (Digilab, Div. FTS 155) instrument with a wave number accuracy of $\pm 4 \text{ cm}^{-1}$. All the spectra presented in this study are difference spectra. The sizes of Au particles were determined in a transmission electron microscope. BET measurements were carried out by N_2 adsorption at 77 K. Catalytic measurements were carried out in a fixed bed continuous flow reactor made of a quartz tube. The flow rate of reactant gases was 12 ml/min. The exit gas was analyzed by gas chromatograph (Hewlett-Packard 5890) on a Porapak QS column. The carrier gas was Ar which contained 12.5% of C_3H_8 . In the study of $\text{CO}_2 + \text{C}_3\text{H}_8$ reaction we applied a gas mixture of 1:1 mole ratio. The selectivity for C_3H_6 was calculated as follows: $\text{C}_3\text{H}_6 \text{ selectivity} = 3 \times n_{\text{C}_3\text{H}_6} / \sum_i x_i n_i \times 100$. In the temperature programmed desorption (TPD) and temperature programmed reduction (TPR), the heating rate was 5 K/min and the flow of Ar (TPD) and H_2 (TPR) was 20 ml/min. The products desorbed or formed were determined by gas chromatograph.

3. Results

3.1. Characterization of the catalysts

The main size of the Au particles in the Au/ZnO is small, 2–3 nm, and uniform. This value for Au/MgO and Au/ Al_2O_3 falls in the range of 2–10 nm. BET surface area of the catalysts used is as follows: 50 m^2/g for Au/ZnO, 170 m^2/g for Au/MgO and 100 m^2/g for Au/ Al_2O_3 . All catalysts have been also characterized by X-ray photoelectron spectroscopic measurements (XPS). In the analysis of the XPS spectra we accepted the BEs of three Au states: 84.0 eV for Au^0 , 84.6 eV for Au^{1+} and 85.9 eV for Au^{3+} . Binding energies obtained fell in the range of 84.1–84.3 eV suggesting that Au is in the form of Au^0 . Some characteristic data for supported Au are shown in Table 1.

3.2. IR spectroscopic studies

The adsorption of propane on Au/ZnO catalyst was performed around 215 K. FTIR spectra obtained are presented in Fig. 1A. Note that the gas-phase spectrum has been subtracted from each spectrum. At $\sim 215 \text{ K}$ absorption bands can be identified at 2981, 2967, 2960, 2901, 2875 cm^{-1} in the high frequency region, and 1472, 1457, 1387, 1375 cm^{-1} in the low frequency range. Heating the sample to 373 K, or adsorption of propane at 373 K led to a dramatic attenuation of all bands occurred with slight shifts in their position. In the low frequency region the absorption bands emerged only at higher temperature. Absorption bands observed at different temperatures and their possible assignments are shown in Table 2.

3.3. TPD measurements

The interaction of propane with Au/ZnO catalysts and ZnO support was also examined by means of TPD measurements. The sample was kept in the propane flow for 15 min at 300 K, and then it was washed with pure Ar until it contained propane (~ 15 –

20 min). TPD spectra are displayed in Fig. 1C and D. No weakly adsorbed C_3H_8 was detected, it desorbed very likely when washing the catalysts with Ar before TPD measurements. From pure ZnO the desorption of larger amount of CH_4 with $T_p = 773 \text{ K}$, and the release of smaller amounts of C_2H_4 and C_2H_6 also above 700 K were registered. In the case of Au/ZnO catalyst almost twice as much CH_4 desorbed also with $T_p = 773 \text{ K}$.

3.4. Dehydrogenation of C_3H_8

Conversion of propane on various Au samples as a function of reaction temperature is given in Fig. 2A. Au/ Al_2O_3 and Au/MgO exhibited a very slight catalytic effect even at 873 K. A much higher activity was found on Au/ZnO. The reaction started above 725–750 K and the conversion of propane reached 17% at 873 K. The catalyst exhibited a remarkable stability. To establish the contribution of the Au similar experiments were performed with ZnO support alone. ZnO also catalyzed the dehydrogenation reaction, but the conversion of propane was much less, 8%, than that measured on Au/ZnO catalyst. The major products on ZnO and Au/ZnO are H_2 followed by C_3H_6 , CH_4 and C_2H_4 . Product distributions obtained on different catalysts are presented in Fig. 3. The selectivity for C_3H_6 formation on Au/ZnO is in the range of 83–90%. On the catalysts showing a low activity the product distribution is somewhat different.

3.5. Reaction of $\text{CO}_2 + \text{C}_3\text{H}_8$

Adding CO_2 to propane caused only a slight increase in the extent of the reaction of C_3H_8 on Au/MgO and Au/ Al_2O_3 . CO_2 enhanced only moderately the extent of the reaction of propane on pure ZnO used for the preparation of Au/ZnO: the conversion of C_3H_8 reached only 13% at 873 K. A dramatic increase occurred, however, on Au/ZnO catalyst. The reaction started even at 650 K. The conversion of C_3H_8 approached 50% at 873 K (Fig. 2B). Similar conversion values were obtained for CO_2 (Fig. 2C). The product distribution also underwent a significant change. The reaction occurring between CO_2 and C_3H_8 is indicated by the formation of significant amount of CO, which exceeded even that of C_3H_6 . This is shown in Fig. 4. Apart from the CO, CH_4 became the major product followed by H_2 , C_3H_6 and C_2H_4 . The experiments have been repeated by three times using always a fresh catalyst. The conversion value fell in the range of 45–50% and we obtained the same sequence of products with only a slight variation. The approximate error bars $\pm 3\%$. Note that we did not experience a decrease in the activity of Au/ZnO at 873 K for several hours, but it drastically declined when the reaction temperature was raised above 923 K. The selectivity of C_3H_6 formation was the highest, 70–75%, at 773 K. This value became lower, 56.3%, at 873 K. However the yield of C_3H_6 production considerably increased from the value of 6–7 (773 K) to a value of 25–30 (873 K). A great effort was made to identify the formation of hexane and hexene, the products of dimerization of C_3H_7 and C_3H_6 species. Both compounds were detected only in trace quantities.

Table 1
Characteristic data for the catalysts and for the reactions of propane.

Catalyst	Surface area, m^2/g	Average size of Au particles, nm	BE values (eV) of the Au	Conversion of C_3H_8 (%) at 873 K		Formation of H_2 , nmol/gs At 873 K	Selectivity of C_3H_6 , %
				In the absence of CO_2	In the presence of CO_2		
Au/ZnO	50	2–3	84.1	16.5	50	1060	56
Au/ Al_2O_3	100	2–10	84.3	4.2	4.9	5.0	35
Au/MgO	170	2–10	84.2	1.3	1.9	1.9	44
ZnO	60	–	–	8.0	13	21	62

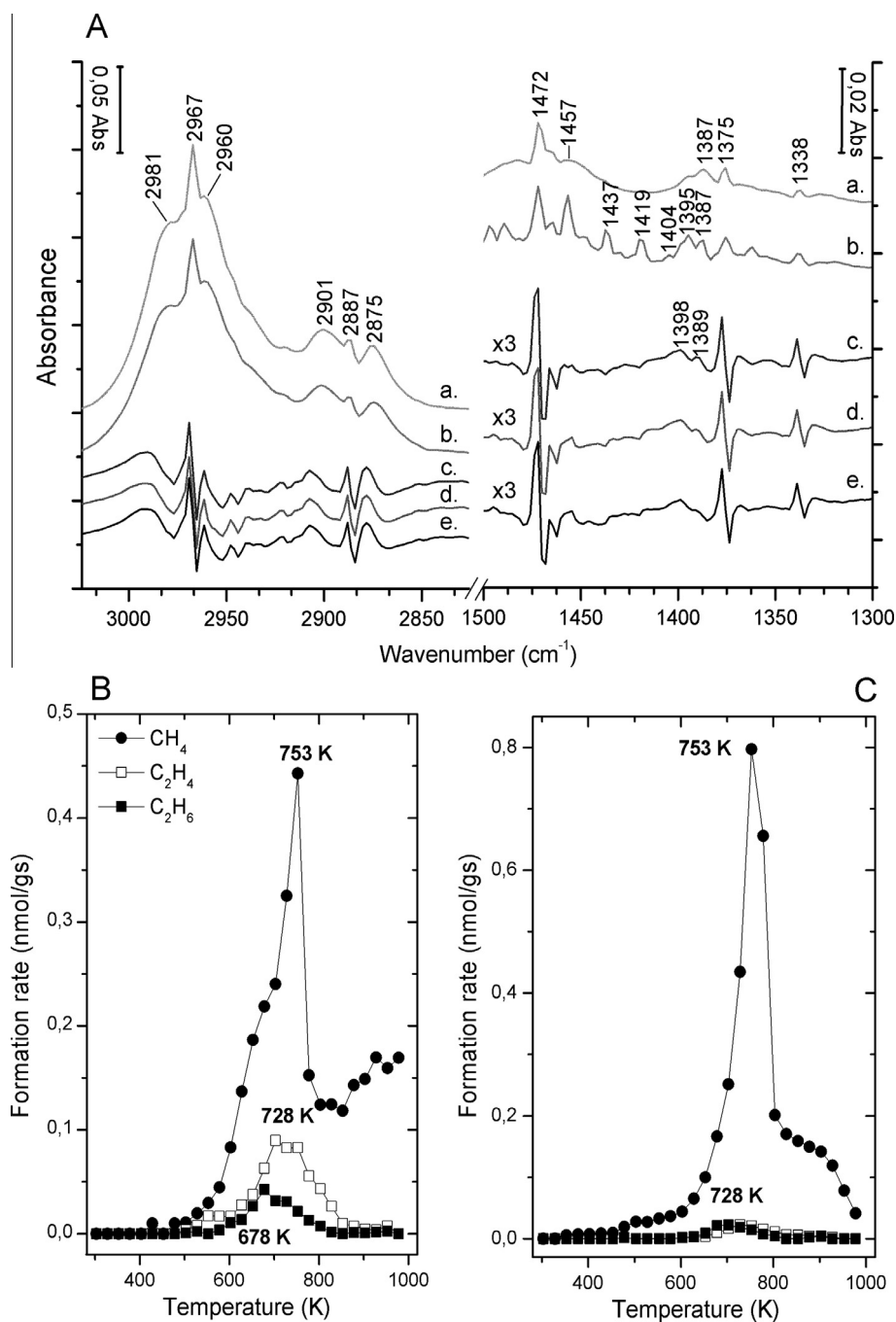


Fig. 1. (A) Infrared spectra of adsorbed C₃H₈ on Au/ZnO at different temperatures: (a) 215 K; (b) 273 K; (c) 373 K; (d) 573 K; (e) 873 K. TPD spectra of C₃H₆ following its adsorption on ZnO (B) and Au/ZnO (C).

When the amount of CO₂ is varied keeping the concentration of C₃H₈ constant, the extent of reaction of C₃H₈ at lower CO₂ content decreased. An increase in the CO₂:C₃H₆ ratio only slightly enhanced the conversion of C₃H₈ and altered only little the product distribution. Results obtained are plotted in Fig. 5A and B. The apparent activation energies for the formation of different products have been determined on Au/ZnO in the temperature range of 763–823 K. Some Arrhenius plots are displayed in Fig. 5C. We obtained the following values: 105.5 kJ/mol for C₃H₆; 129.6 kJ/mol for CO; 161.3 kJ/mol for H₂ and 186.7 kJ/mol for CH₄.

The amounts of carbon-containing deposit formed in the CO₂ + C₃H₈ reaction on Au/ZnO catalyst and its reactivity have

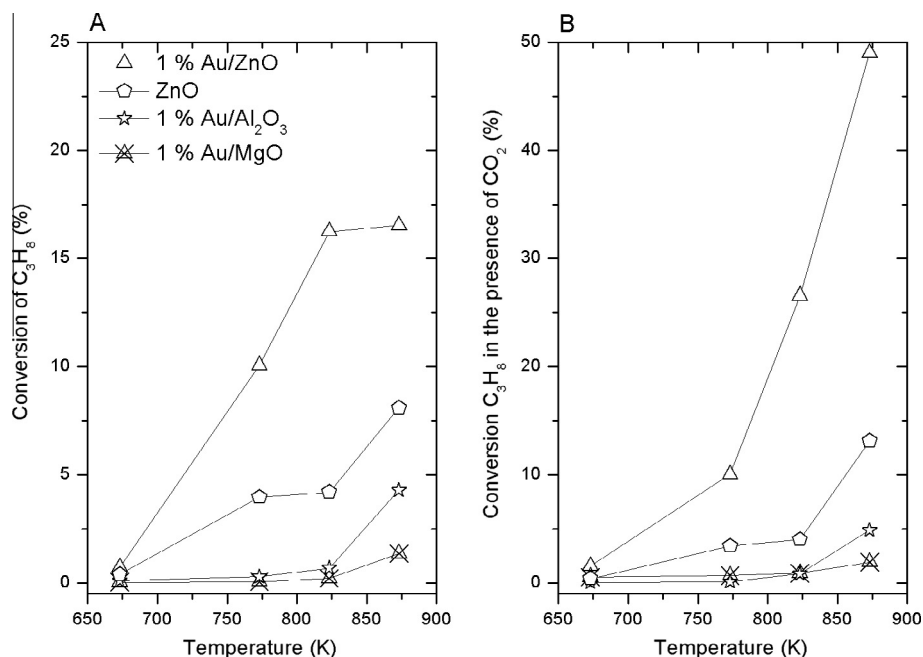
been determined by TPR measurements. The formation of methane, ethylene and ethane was established. Methane peak was found at T_p = 874 K, but its continuous evolution was experienced even above this temperature. The formation of C₂H₆ occurred in two peaks with T_p values of 841 and 1039 K, while that of C₂H₄ with T_p ≈ 872 K and 1118 K. TPR spectra are displayed in Fig. 6.

One of the referees noted that the carbon mass balance is very important, particularly when the conversion exceeds 70%. Although the conversion in our case was always below 50%, we calculated the carbon balance for all measurements performed on Au/ZnO. About 6–11% of C was missing in average, which was

Table 2

Characteristic vibrations and their assignments observed for gaseous and adsorbed propane.

Assignment	Gas	Rh/SiO ₂ 173–193 K [8]	Au/ZnO 215–273 K [present work]	Rh/SiO ₂ 300 K [8]	Au/ZnO 373 K [present work]
$\nu_{as}(\text{CH}_3)$	2977	2960	2981	2964 (II)	2969 (II)
$\nu_{as}(\text{CH}_3)$	2973		2967	2926 (II, III)	2962
$\nu_s(\text{CH}_3)$	2962	2940	2960	2898 (II, III)	2907 (II, III)
$\nu_{as}(\text{CH}_2)/\nu_{as}(\text{CH}_3)$	2968	2904	2901	2877 (I)	2899 (I)
$\nu_s(\text{CH}_2)/\nu_{as}(\text{CH}_3)$	2887	2876	2875	2868 (II, III)	2887
$\delta_{as}(\text{CH}_3)$	1476				
$\delta_{as}(\text{CH}_3)$	1472	1486		1490 (II, III)	1472 (II, III)
$\delta_{as}(\text{CH}_3)$	1464		1472	1450 (II, III)	1457 (II, III)
$\delta(\text{CH}_2)$	1462	1448	1457		
$\delta_s(\text{CH}_3)$	1392	1387	1387	1382 (II, III)	1389 (II, III)
$\delta_s(\text{CH}_3)$	1378	1371	1375	1354 (III)	1375
$\omega(\text{CH}_2)$	1338	1335			1342

Note: I π -bonded propylene; II di- σ -bonded-propylene; III propylidene.**Fig. 2.** Conversion of C_3H_8 in its dehydrogenation (A) and in the $\text{CO}_2 + \text{C}_3\text{H}_8$ reaction (B) on various catalysts at different temperatures.

attributed to the low reactivity of the carbon deposit formed in the reaction at 873 K.

3.6. Reactions of propylene

In order to find out the fate of propylene formed in the decomposition propane, its reaction with CO_2 was also examined on Au/ZnO. Propylene underwent relatively little decomposition over this catalyst. The conversion reached only 4.5% at 873 K. The main product was H_2 . Less amount of CH_4 was also detected. Adding CO_2 to C_3H_6 increased the conversion with few percents and led to the formation of CO. An enhanced formation of CH_4 also occurred, which exceeded that of H_2 . Raising the temperature above 823 K caused a decline of the conversion of C_3H_6 .

4. Discussion

4.1. IR spectroscopic studies

The interaction of propane with supported Rh [8], Re [9] and Mo_2C [10] catalysts has been investigated before by means of FTIR spectroscopy. Adsorption of propane on Au/ZnO at 200–215 K

caused the appearance of intense absorption bands at 2981, 2967, 2960, 2901, 2875 cm^{-1} in the CH stretching region and 1472, 1457, 1387, 1375 cm^{-1} in the low frequency range. The spectrum shows a good agreement with those obtained on other catalysts at low temperature [20–25]. These absorption bands are characteristic for molecularly adsorbed propane, and their assignments are presented in Table 2. Although the catalytic reactions of propane proceed at high temperatures (Figs. 2 and 3) changes in the IR spectra indicate the occurrence of a surface interaction at or above room temperature. As in the previously studied catalysts, the formation of π -bonded propylene, di- σ -bonded propylene and propylidene is postulated (Table 2). These adsorbed species appear to be strongly bonded to the catalysts surface, as no change was experienced in the IR spectra even at high temperatures.

TPD measurements showed that a fraction of strongly adsorbed C_3H_8 remained on both the ZnO and Au/ZnO. It decomposed only above 700 K resulting in the formation of CH_4 , C_2H_6 and C_2H_4 .

4.2. Catalytic studies

The dehydrogenation of propane

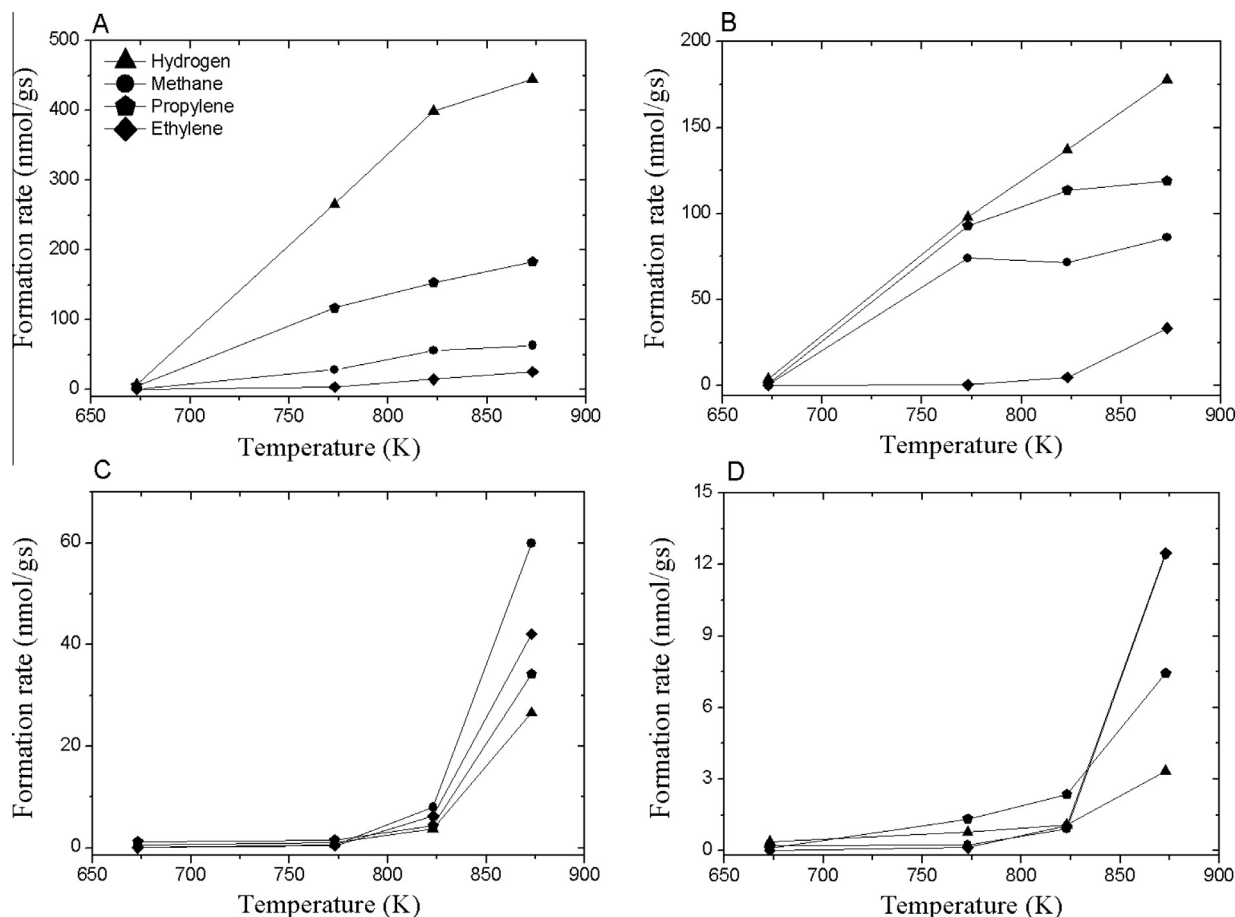
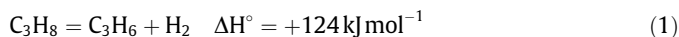


Fig. 3. Product distribution in the dehydrogenation of C_3H_8 on various catalysts at different temperatures: (A) Au/ZnO; (B) ZnO; (C) Au/ Al_2O_3 ; (D) Au/MgO.



is strongly endothermic and also equilibrium limited. Higher conversion will require either higher temperature or lower pressures. In the case where the feed gas is only propane, the equilibrium propane conversion is given by the formula $K_p = P \cdot x^2 / (1 - x^2)$ with K_p the equilibrium constant, x the equilibrium conversion and P the total pressure.

From the supported Au catalysts examined only the Au/ZnO exhibited a moderate catalytic effect for the dehydrogenation of propane. Au/MgO and Au/ Al_2O_3 were found almost inactive below 873 K. The conversion on Au/ZnO reached a value of 17–18% even at 823 K. We notice that the conversion of the propane never matched with the chemical equilibrium at any temperatures. The amount of H_2 is more than 2 times larger than that of C_3H_6 . Note that we did not experience such a behavior in the case of pure ZnO up to 823 K, when the H_2/C_3H_6 ratio was 1.0–1.3. This indicates that Au nanoparticles are responsible for the large deviation in the amount of H_2 and C_3H_6 . In the explanation of this feature we assume that a significant fraction of C_3H_8 underwent a complete decomposition to carbon



and the C_3H_6 formed in the primarily process (Eq. (1)) also decomposed further



The fact that we found CH_4 and C_2H_4 in the products supports the occurrence of these reactions.

The situation is different when CO_2 was added to C_3H_8 . While CO_2 only slightly increased the conversion of C_3H_8 on pure ZnO (see Fig. 2), it exerted a drastic enhancement in the conversion of C_3H_8 on Au/ZnO. The amounts of all products found in the dehydrogenation of C_3H_8 considerably increased. The fact that a large amount of CO formed clearly indicates the involvement of the CO_2 in the reaction of propane. In light of the formation of products we can account with the dry reforming of propane



and with the oxidative dehydrogenation of propane



An interesting feature of the $CO_2 + C_3H_8$ reaction is the production of a large amount of CH_4 , which was one order of magnitude higher than in the absence of CO_2 . We may assume the occurrence of the extended hydrogenolysis of propane in the presence of a large amount of H_2



However, C_2H_6 was not detected even in traces, which excludes this route of methane formation. In addition this route of CH_4 production does not need the presence of CO_2 . A possible explanation of the extended formation of CH_4 is the hydrogenation of CO_2



Supported Au samples, however, were found to be completely inactive for the above reaction below 500 K [26]. Control measurement performed on the same Au/ZnO catalyst used in the present study revealed that H_2 does react with CO_2 at 723–773 K resulting

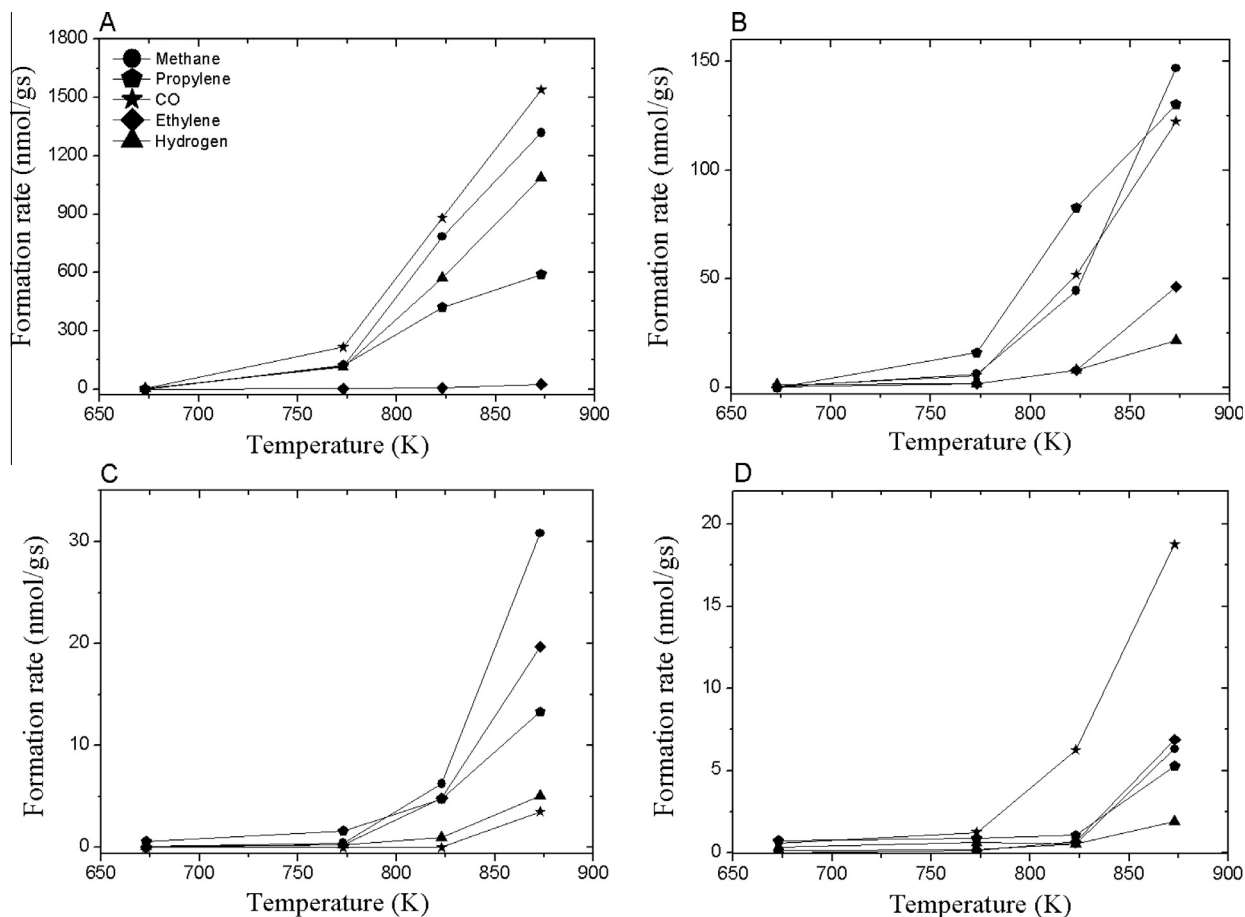


Fig. 4. Product distribution in the reaction of $\text{CO}_2 + \text{C}_3\text{H}_8$ on various catalysts at different temperatures: (A) Au/ZnO; (B) ZnO; (C) Au/ Al_2O_3 ; (D) Au/MgO.

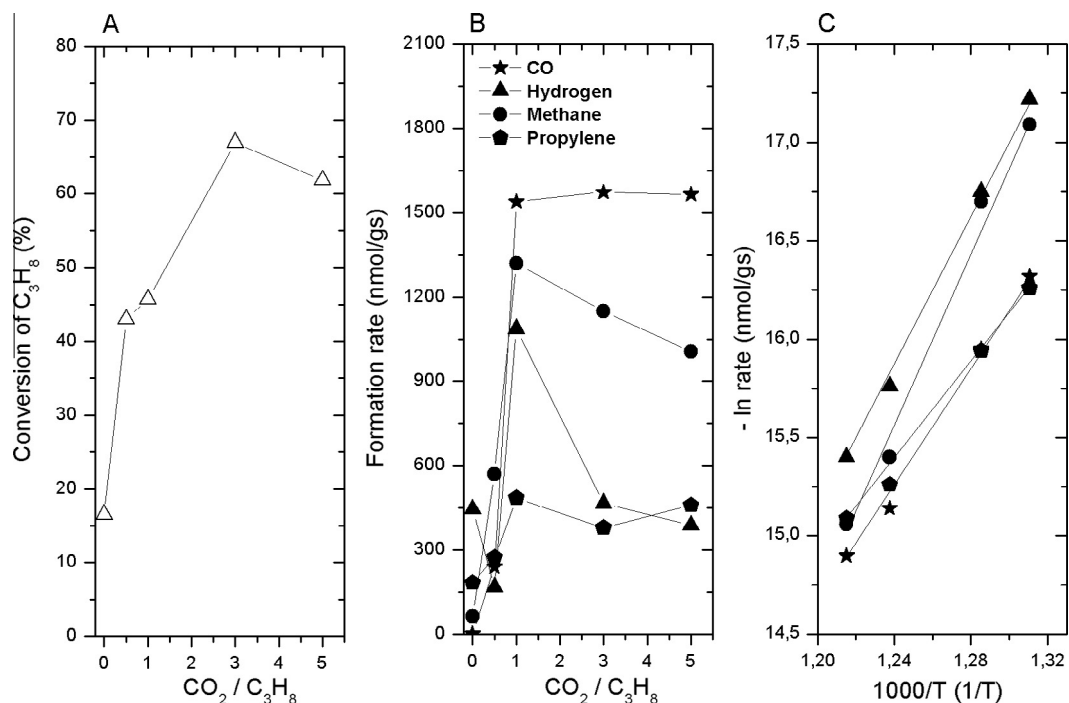


Fig. 5. Effects of $\text{CO}_2/\text{C}_3\text{H}_8$ ratio on the conversion of C_3H_8 (A), and on the formation of various products on Au/ZnO at 823 K (B). Arrhenius diagram for the formation of different products on Au/ZnO (C).

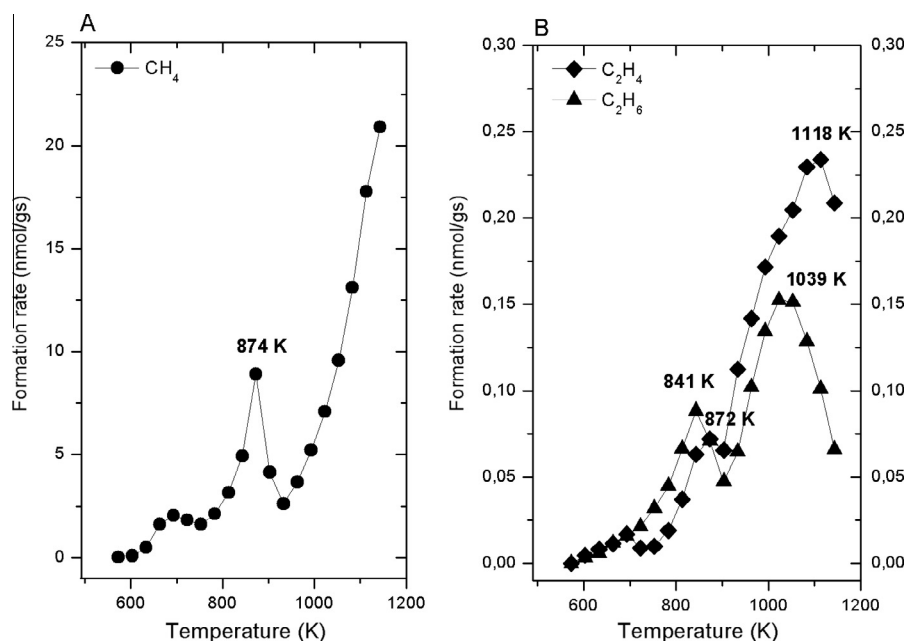
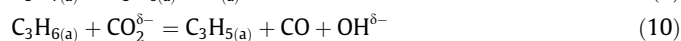
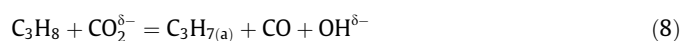


Fig. 6. TPR spectra following the $\text{CO}_2 + \text{C}_3\text{H}_8$ reaction on Au/ZnO at 873 K.

only in CO and H_2O . Methane was detected only in a very small quantity. Similarly, we found no methane formation in the hydrogenation of CO on the same catalyst. Accordingly, we may assume that CH_4 is formed in the decomposition of C_3H_5 radical (see below, Eq. (11)).

In the explanation of much greater activity of Au/ZnO compared to Au/ Al_2O_3 and Au/MgO we should take into account that ZnO is an n-type semiconductor, while Al_2O_3 and MgO are insulating oxides. Based on the work function of ZnO (3.95–4.25 eV) and Au (~5.3 eV), we expect an electronic interaction between Au and ZnO, e.g. an electron transfer from ZnO to Au particles at the Au/ZnO interface [27]. This may result in the activation of rather inert CO_2 on Au particles in the form of negatively charged CO_2^- . It has been demonstrated in several studies that negatively charged CO_2 is much more reactive than the neutral one [28,29]. Recently, it was reported that n-type oxidic supports for Au are much more efficient in the reaction between CO_2 and C_2H_6 compared to Au samples deposited on insulating oxides [19].

In light of this consideration we describe the $\text{CO}_2 + \text{C}_3\text{H}_8$ reactions with following elementary steps. We assume that the partially negatively charged CO_2 enters reaction with the stable hydrocarbons, C_3H_8 and C_3H_6 , producing more reactive C_xH_y fragments



Accordingly CH_4 can be formed in the decomposition of C_3H_7 radical (Eq. (11)).

In the study of the reactions of C_xH_y fragments over metal single crystals in UHV it was found that a fraction of C_xH_y species is dimerized beside their decomposition [30–33]. In the case of C_3H_7 hexane (C_6H_{14}) and hexene (C_6H_{12}) were identified. This process was more expressed on less reactive Au(111) [30,31] compared to Rh(111) [32] and $\text{Mo}_2\text{C}/\text{Mo}(100)$ [33] surfaces. In the

present study we found no sign of the formation of these compounds. The possible reason is that the reaction of propane occurred at very high temperature, above 650 K, when the favorite route of the C_3H_7 and C_3H_5 is their decomposition.

We may compare the catalytic performance of supported Au in the $\text{CO}_2 + \text{C}_3\text{H}_8$ reaction with other catalysts examined under exactly the same experimental conditions. A general feature is that CO_2 markedly accelerated the reaction of C_3H_8 on all catalysts. Over Al_2O_3 -supported Pt metals the dehydrogenation of propane occurred at 823–923 K with selectivities of 40–55% [5]. The activity of the catalysts depended on the nature of the metal: on the most effective Rh/ Al_2O_3 , the conversion reached a value of 63.5%, and on the less effective Pd/ Al_2O_3 this value was only 4.3%. These catalysts were found to be effective for the dry-reforming of propane to produce synthesis gas at 823–923 K [5]. Over Re/ Al_2O_3 the decomposition of C_3H_8 sets in at 873–923 K with selectivity to propylene of 43–74% [9]. Adding CO_2 to C_3H_8 changed the reaction pathway of C_3H_8 , and the dry reforming of C_3H_8 came into prominence. Mo_2C deposited on SiO_2 catalyzed the dehydrogenation of C_3H_8 at 773–873 K [10]. The selectivity of propylene formation attained a value of 35–50% at a conversion of 25–35%.

5. Conclusions

- (i) Propane interacts with Au/ZnO even below 300 K yielding adsorbed propylene and propylidene.
- (ii) Dehydrogenation of C_3H_8 and its reaction with CO_2 are limited on Au/MgO and Au/ Al_2O_3 .
- (iii) In contrast, Au/ZnO exhibited a much higher activity in the dehydrogenation of propane. Adding CO_2 to propane further increased the conversion.
- (iv) The catalytic performance of Au/ZnO was explained by the occurrence of an electronic interaction between Au and n-type ZnO leading to the activation of CO_2 .

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